

## Description

## 5 Process for producing thermochemically modified starch

10 The present invention is in the technical field of physicochemical starch modification and relates to a process for the thermochemical modification of starch, the acid-modified starches which are obtainable by the inventive process and have thin-boiling to thermally reversible gel-forming properties, and to their use.

Conventional starches obtained by acid modification, for example thin-boiling starches, are generally produced using what is termed a "slurry" process. In this process the aqueous suspension of a starch is stirred for a number of hours in the presence of mineral acid (for example HCl, H<sub>2</sub>SO<sub>4</sub> or H<sub>3</sub>PO<sub>4</sub>) below its pasting temperature, then neutralized, washed, dewatered and finally dried (Whistler & Pashall: Starch: Chemistry and Technology Vol. II, Academic Press, New York and London, 1969, p. 219).

20 A starch modified in this manner, compared with the native comparison sample, shows a reduced thickening power on heating and an intensified gel-formation tendency after cooling. The modified property profile of this modified starch opens up numerous technical applications, inter alia in the food sector.

25 The use of acid-modified starch is gaining increasing importance in the food industry. Acid-modified starches are used especially to produce foods, in particular confectionery products, for example as substitutes for gelatin and gum arabic. However, there are also possible applications in industrial sectors, for example in yarn finishing in textile manufacture and in papermaking to improve abrasion  
30 resistance and printability.

In addition to the known "slurry" processes (see above), Klingler et al. have described a "semi-dry" process for producing acid-modified green-pea starch (Klingler et al., Starch/Stärke 1997, 49, 391-395), which not only produces thin-boiling starches, but also leads to a high-grade thermally reversible gel-forming dextrin product. Advantages of the process described compared with the slurry process are, for example, the lower chemical usage, a shorter reaction time, the reduction of byproducts and product losses and the avoidance of wastewaters and their disposal.

Disadvantages of the process described are the insufficient quantitative availability of green-pea starch, which is reflected in its economic efficiency, and in the limited spectrum of properties of the acid-modified green-pea starches.

The object of the present invention is therefore to provide by alternative means high-grade thermochemically modified starches which overcome the abovementioned disadvantages and conform to the various industrial requirements with respect to their properties.

Surprisingly, it has now been found that, by means of the inventive thermochemical process described in more detail in the claims, high-grade thin-boiling starches and, moreover, reversible gel-forming dextrans can be economically provided in sufficient quantity and a broad variability of properties of the obtainable products can be achieved. The inventive process therefore offers all of the abovementioned economic and ecological advantages of a semi-dry process.

By means of the present invention, to this extent, a surprisingly simple and economic alternative to the known production processes for thermochemically modified starch is provided, which can be used in a versatile manner.

Surprisingly, the inventive acid-modified thin-boiling starches and the thermally reversible gel-forming dextrans have a granular structure which leads to a very high dispersibility in contrast to commercially available reversible gel-forming dextrans.

- 5 The present invention therefore relates to a process for the thermochemical modification of starch, with the exception of green-pea starch, in which
- a) starch having a moisture content of a maximum of about 15-20%, preferably less than 10%, is heated in the presence of an acid at a rate of at least 3 K/min, especially 3-200 K/min, preferably about 4-200 K/min, in particular about 5-100 K/min, particularly preferably about 10-100 K/min, to a temperature no higher than about 50-120°C, preferably no higher than about 65-110°C, in particular no higher than about 80-100°C, and
  - b) the pH is then neutralized, preferably set to a pH of about 5.5-7.5, in particular 6.0-6.5.

In a preferred embodiment, in the inventive process, before or during the neutralization, the temperature specified in process step a) is held for a period of up to 1 hour, preferably up to 30 minutes, and in particular up to 20 minutes.

In a further embodiment of the inventive process, after reaching the temperature specified in process step a), or after the neutralization, the starch is cooled at a rate of up to 10 K/min, preferably up to 5 K/min.

In a particular embodiment of the inventive process, the starch is heated at a rate of about 3-50 K/min, preferably 4-50 K/min to a temperature of about 60-120°C, preferably of about 90-120°C and is then neutralized.

A further embodiment of the inventive process serves in particular to produce thin-boiling starch, in which, in process step a) of the inventive process, the starch is heated to a temperature which is between the pasting temperature and 15°C above the pasting temperature of the starting starch.

A still further embodiment of the inventive process serves especially to produce thermally reversible gel-forming dextrans, in which, in process step a), the starch is heated to a temperature more than about 15-50°C, preferably more than about 15-30°C, in particular more than about 20-25°C, above the pasting temperature of the starting starch.

In a further preferred embodiment of the inventive process, thermally reversible gel-forming dextrans may be produced by choosing in step a) an acid concentration of about 40-100 mmol of acid/kg of starch, preferably about 50-80 mmol of acid/kg of starch and, if appropriate, heating the starch at a rate of about 15-100 K/min, preferably about 30-100 K/min.

The term „starting starch“ here designates the starch which is subjected to the thermochemical treatment in the inventive process, with the exception of green-pea starch.

Suitable possible heating methods are, for example, using heating devices known to those skilled in the art, in which, in particular, heating of the starch to temperatures above 120°C is to be avoided. Microwave ovens appropriately provided with a stirring apparatus have proved useful for this, but other heating devices known to those skilled in the art are also suitable. Alternatively, one or more of the reactants (starting starches, acid or alkali) can also be heated in a suitable manner before they are brought into contact with one another, so that if appropriate no heating power, or only a small amount of heating power, is required during the reaction. The process can proceed, in particular, in a continuous process so that technical problems during the heating of relatively large amounts of starch can be avoided. The possibilities of a continuous process procedure suitable for this are well known to those skilled in the art.

In the inventive process, in a further embodiment for accelerating the starch-hydrolysis reaction, the heating can be carried out with slight pressure elevation. The pressure range suitable for the inventive process is at the maximum up to 5 bar (500 kPa).

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Optionally, the inventive process can be carried out in the presence of an alcohol, preferably methanol, ethanol, 1-propanol and/or 2-propanol, or in the presence of a suitable mixture of water and alcohol.

10 The starting starches used in the inventive process for producing thermochemically modified starch are preferably starches from starch-storing plants, in particular from the group consisting of corn, wheat, tapioca, mung bean and potato. In addition to the customarily available starches from naturally existing plants, recently, starches from plants are increasingly becoming available which have been produced by mutant selection or by genetic engineering methods and which may have been modified, for example, with respect to their quantitative or qualitative starch content (gently modified starches). In particular, owing to these processes, starches are available from corn, potato and wheat which, for example, are increased in their amylose content and/or, with respect to their degree of phosphorylation, have  
20 markedly modified properties. Starches of this type are explicitly suitable as starting starches in the inventive process.

By way of example, genetically modified starches are disclosed by the patent literature mentioned below, with the publications mentioned representing an arbitrary  
25 enumeration, and not representing a preferred or complete selection:

WO 90/12876A1, WO 91/19806A1, WO 92/11375A1, WO 92/11376A1,  
WO 92/11382A1, WO 92/14827A1, WO 94/09144A1, WO 94/11520A1,  
WO 95/04826A1, WO 95/07355A1, WO 95/26407A1, WO 95/34660A1,  
WO 95/35026A1, WO 96/15248A1, WO 96/19581A1, WO 96/27674A1,  
30 WO 96/34968A1, WO 97/04112A1, WO 97/04113A1, WO 97/11188A1,  
WO 97/16554A1, WO 97/20040A1, WO 97/22703A1, WO 97/45545A1,

WO 98/11181A1, WO 98/15621A1, WO 98/37213A1, WO 98/37214A1,  
and CA 2,061,443, DE 19820607.0, DE 19820608.9, DE 19836097.5,  
DE 19836098.3, DE 19836099.1, EP-A-0 521 621, EP-A-0 703 314,  
EP-A-0 737 777, EP-A-0 779 363 or US 5,300,145.

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It is particularly surprising that, using the inventive process, outstanding products,  
that is to say thermochemically modified starches, are also obtained if starting  
starches having an amylose content less than 30% (w/w) are used. However, in  
addition, starches having an amylose content greater than 40% (w/w) are a further  
10 preferred selection range of suitable starting starches which lead to products of very  
high quality grade.

The acids used in the inventive process for producing thermochemically modified  
starch are generally organic or inorganic acids, preferably mineral acids, for example  
15 HCl, H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub> or H<sub>3</sub>PO<sub>4</sub>. The use of acids having a somewhat weaker pK<sub>a</sub> of up  
to 2.5 is also highly suitable, however.

The starch in the inventive process is generally thermochemically treated directly or  
indirectly, so that a mild hydrolysis of the glycosidic bonds in the starch molecules is  
20 allowed. In the simplest case, this is made possible by spraying a dilute solution of  
the acid uniformly onto the starch. If appropriate, the acid can also be brought into  
contact in the gaseous state with the starch; it is especially important that a uniform  
and mild hydrolysis is carried out and excessive local acid concentration is avoided,  
since this would otherwise impair the product quality.

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To ensure mild hydrolysis conditions, the acid should therefore generally not be too  
highly concentrated. The acid should be used, or brought into contact with the  
starch, for example as dilute solution at a concentration of about 0.05-5 M,  
preferably about 0.1-3 M. The starch in this case can preferably be mechanically  
30 agitated (stirred, shaken, circulated, etc.), in order to avoid local overconcentration  
of the acid. The acid can be brought into contact with the starch if appropriate warm,

hot, close to boiling point or, if appropriate, in the gaseous state, in order to promote the process and/or product properties, in order to shorten the reaction time, for example.

- 5 Generally, the quantitative ratio of acid to starch in the inventive process is about 1-100 mmol of acid/kg of starch, preferably about 5-75 mmol/kg, in particular about 10-60 mmol/kg.

To complete the reaction, that is to say the acid hydrolysis, in step b) of the inventive process neutralization is carried out using a suitable alkali, if appropriate with cooling, with basic substances suitable for applications in the food sector being preferred. For example, in addition to dilute solutions of NaOH, especially soda solutions in the range of about 0.01-5 M, preferably about 0.05-2 M can be used in the food sector. During the neutralization or after neutralization, the reaction mixture is cooled to a temperature between about 0 and 35°C.

If wanted, the product obtained from the inventive process, that is to say the thermochemically modified starch, can be dried after neutralization, for example by pneumatic drying or fluidized bed drying, or by other suitable drying methods known to those skilled in the art.

Further subject-matter of the invention is also thermochemically modified starches obtainable by the inventive process, in particular those which have a granular structure, and very particularly thermochemically modified corn starch, wheat starch, tapioca starch, mung bean starch and/or potato starch, particularly having a granular structure. Thin-boiling starches, dextrans having a pronounced gel-formation property and thermally reversible gel-forming dextrans which are obtainable by the inventive process are preferred in particular. In a further preferred embodiment, the inventive thermochemically modified starches have a granular structure.

Further subject-matter of the invention is also the use of starch, with the exception of green-pea starch, in the inventive process for producing thermochemically modified starch, in particular the use of corn starch, wheat starch, tapioca starch, mung bean starch and/or potato starch, especially for producing dextrans of granular structure.

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The thermally reversible gel-forming dextrans obtainable from the inventive process are, owing to their special property of the thermally reversible sol-gel transition, outstandingly suitable in certain foods or food compositions (mayonnaises, dressings, ice cream , etc.), e.g. as fat substitutes.

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Still further subject matter of the invention is the use of the inventive thermochemically modified starch for producing foods, food compositions or food intermediate products and the use of the inventive thermochemically modified starch as substitute for fat (for example in foods such as margarine, mayonnaise, dressings, ice cream, peanut butter, coffee whitener, etc.) or as substitute for gelatin, for example in the pharmaceutical sector (gelatin capsules , etc.), or in the food sector for meat products (aspic, jus , etc.), for confectionery products (fruit gum, licorice , etc.) or for thickening and binding delicatessen and dairy products (jelly, milk puddings, crèmes). The inventive thermally reversible gel-forming dextrans, in addition to their primary gel-formation properties, have a flavor binding capacity, dispersibility and/or acid stability which is outstanding for these purposes.

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A further embodiment of the present invention is therefore the use of the thermally reversible gel-forming dextrans obtainable from the inventive process as fat substitute, preferably in food, food compositions or food intermediate products.

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The inventive thermochemically modified starches based on potato starch have a very particular taste-neutral behavior, so that their use is particularly preferred for the above-described fields of application in foods.

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Furthermore, therefore, subject-matter of the invention is a food intermediate



product, food or a food composition comprising an inventive thermochemically modified starch, in particular a fat substitute or gelatin substitute, comprising an inventive thermochemically modified starch, particularly a thermochemically modified potato starch.

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Unless stated otherwise, all percentages associated with the present invention are percentages by weight (% w/w).

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The starches or starch samples which are listed below in the following examples and are labeled with a letter have the following meanings:

A = native starch from potatoes of cultivar Désirée (wild type)

B = starch from genetically modified potatoes, for example obtainable according to Example 10 of WO 97/11188

C = starch from genetically modified potatoes, for example obtainable according to Example 7 of WO 97/11188

D = corn starch, Cerestar, Krefeld, Germany

E = wheat starch, Crespel & Deiters, Ibenbüren, Germany

F = tapioca starch, Thai World Import & Export Co., Ltd

G = amylomaize starch, Hylon V, Nat. Starch & Chemical GmbH, Neustadt, Germany

H = mung bean starch, SitThi Nam Co, Ltd. Sathorn Thani, Bangkok, Thailand

K = potato starch, Emsland Stärke GmbH, Emlichheim, Germany.

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The examples below are intended to illustrate the invention and in no way represent a restriction of the invention.

#### Example 1: Production of thin-boiling starch

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To produce thin-boiling starch, about 150 g of the different starch samples described in more detail below were sprayed with 3-9 ml of 1 M HCl, that is to say 20-60 mmol/kg of starch, with constant mixing, and were heated in a microwave

oven at about 250 W nominal power with stirring to 60-95°C in the course of about 1-2 minutes. The samples were then neutralized with 2-10 ml of a 1 M soda solution and cooled.

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#### Example 2: Viscometric characterization of acid-modified starches

The acid-modified starches produced according to Example 1 were studied by viscometry using a Micro-Amylo viscograph (Brabender oHG, Duisburg, Germany).

10 A commercially conventional product, Perfectagel MPT (Ref. No. 34384/02) from Avebe (Veendam, The Netherlands) served as comparison product.

The Brabender viscosities were determined as follows: 100 g of an 8.5% strength starch suspension were heated with constant stirring at a rate of 3 K/min to 90°C (Table 1A) or the temperature specified, then the temperature was kept constant at 90°C for 15 minutes, then the samples were cooled at 3 K/Min to 30°C and then the change in torque (measurement range 250 cmg) was measured (see Table 1). The viscosities are reported in Brabender units, abbreviated [BU].

20 Table 1A: Viscosity data of various starch samples

	Peak viscosity	Hot paste viscosity <sup>1)</sup>	Cold viscosity <sup>2)</sup>
Perfectagel MPT	130 BU ± 10	20 BU ± 5	100 BU ± 5
Acid-modified starch C (32% amylose)	195 BU ± 10	50 BU ± 5	510 BU ± 10
Starch K, native	2110 BU ± 15	500 BU ± 10	1400 BU ± 10
Acid-modified starch K	300 BU ± 10	50 BU ± 5	340 BU ± 10

<sup>1)</sup> 15 min at 90°C; <sup>2)</sup> 30°C

Table 1B: Effect of modification temperature on viscosity

	Starch B	Heating at			Starch K	Heating at		
	Native [BU]	61°C [BU]	71°C [BU]	80°C [BU]	Native [BU]	62°C [BU]	69°C [BU]	73°C [BU]
Peak viscosity	664	425	332	197	1871	1388	1088	928
Hot paste – <sup>1</sup>	478	267	224	125	454	301	259	209
Cold viscosity <sup>2)</sup>	1377	751	603	317	1304	841	723	632

<sup>1)</sup> 15 min at 90°C; <sup>2)</sup> 30°C

### 5 Example 3: Production of gel-forming dextrins

The individual starch samples listed in Table 2 (below) were dried to about 8-9% moisture content. 100 g of the starch were sprayed in each case with 1-3.75 ml of a 2 M HCl solution (20-75 mmol of acid/kg of starch) and heated in a rotating round-bottomed flask (250 ml) for 5-20 minutes in an oil bath from room temperature (about 23°C) to a temperature of 90-105°C, and then either immediately, or after the hot-holding time mentioned below, neutralized with 1 M soda solution and cooled. For the subsequent characterization of the dextrins, 20% strength boilings at 90°C (Haake Rotovisko RV 12 from Haake, Karlsruhe, Germany) or at 120°C (autoclave type KL 51 from Wolf) were charged into cylindrical vessels of two rings one above the other (each 20 mm high, diameter 25 mm), stored for one day at room temperature (23±2°C) and then the gel firmness was measured. The gel firmness was measured after about 24 hours of storage at room temperature using a texture analyzer (TA.XT2 Stable Micro Systems, Haslemere Surrey GU27 3AY, Great Britain) by single compression of the gel using a flat-ended cylinder probe (diameter 24.5 mm). A planar gel surface was obtained by slicing through the solidified gel between the two rings. The thermal reversibility of gel formation was tested by melting, and the appearance (color, glossiness), consistency (paste-like) and homogeneity and taste were assessed.

Tables 2 A-D show the dextrin properties with respect to gel firmness, thermal reversibility of gel formation and also their optical appearance.

- 5 Gel firmness values in a range of about  $5 \pm 3$  N indicate a gel firmness generally suitable for a fat substitute. Highly suitable fat substitutes are distinguished, furthermore, by a color as white as possible, a glossy surface, a homogeneous fatty consistency and a thermally reversible gel formation.

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Table 2: Effect of differing process parameters on dextrin properties

Table 2A: 20 mmol HCl/kg of starch

	T [°C]	95			100			105
Starch sample	Holding time [min]	0	5	10	0	5	10	0
	Gel firmness [N]	7.7	5.2	6.5	4.1	6.2	0.8	
D	Optical properties	whiteish yellow	whiteish yellow	whiteish yellow	whiteish yellow	thermally rev	thermally rev	
	Gel firmness [N]	n.m.	5.5	4.8	n.m.	0.5	0.4	
E	Optical properties	white transparent	white- transparent matt	white- transparent matt		white- transparent glossy	white- transparent glossy	
	Gel firmness [N]				n.m. too solid	n.m.	28.5	28.3
B	Optical properties						white transparent	gray

Table 2B: 30 mmol HCl/kg of starch

Starch sample	T [°C]	95				100			
		0	5	10		0	5	10	
D	Holding time [min]								
	Gel firmness [N]	1.3 thermally rev	1.9 thermally rev	n.m. too thin		0.2 thermally rev	n.m. too thin	n.m. too thin	
E	Optical properties	Whiteish-yellow	whiteish-yellow			whiteish-yellow			
	Gel firmness [N]	1.0 thermally rev	n.m. too thin	n.m. too thin		0.7 thermally rev	0.4 thermally rev	0.4 thermally rev	
F	Optical properties	white-transparent glossy				white transparent	white glossy	white glossy	
	Gel firmness [N]					3.9 thermally rev	1.2 thermally rev	n.m. too thin	
	Optical properties					whiteish-brown transparent	whiteish-brown transparent		

	T [°C]	95				100				105			
Starch sample	Holding time [min]	0	5	10	0	5	10	0	5	10			
A	Gel firmness [N]	27	9	5	9.2	n.m.	n.m.						
		thermally rev	thermally rev	thermally rev	thermally rev	too thin	too thin						
	Optical properties	white glossy	white glossy	white glossy	white glossy								
B	Gel firmness [N]				1.75	24.2	6.2	1.6	17.4	8.4			
					thermally rev	thermally rev	thermally rev	thermally rev	thermally rev	thermally rev			
	Optical properties				white glossy	gray	white glossy	white glossy	gray	white glossy			
D	Gel firmness [N]					0.4	n.m.	n.m.					
							too thin	too thin					
	Optical properties					whiteish-yellow							

Starch sample	T [°C]	95				100			105		
		0	5	10		0	5	10	0	5	10
G	Holding time [min]										
	Gel firmness [N]						2.5	thermally rev	0.9	thermally rev	n.m. too thin
E	Optical properties						whiteish- yellow glossy		whiteish- yellow glossy		
	Gel firmness [N]						0.5	thermally rev	0.6	thermally rev	n.m. too thin
H	Optical properties						white- transparent glossy		white- transparent glossy		
	Gel firmness [N]						9.1	thermally rev	1.0	thermally rev	n.m. too thin
	Optical properties						whiteish- gray matt		whiteish- gray matt		



Table 2D: 60 mmol HCl/kg of starch

Starch sample	T [°C]	100		
		0	5	10
B	Holding time [min]			
	Gel firmness [N]	11.1 thermally rev	1.15 thermally rev	n.m. too thin
	Optical properties	light transparent	white glossy	

Key to Tables 2 A-D:

- n.m. = not measurable (too firm or too soft)
- thermally rev = thermally reversible gel formation

### Example 3B: Effect of heating rate on dextrin properties

According to the description of example 3 commercially available potato starch (starch sample K) was heated with different rates from room temperature (about 23°C) to T= 95°C (without holding time).

Table 2E: Effect of heating rate on dextrin properties

Heating time [min]	Gel strength [N]	Gel properties
15	$8.3 \pm 0.5$	pasty gel, white, thermally reversibel
120	$39.9 \pm 0.1$	solid gel, greyish, irreversibel
150	$32.0 \pm 0.5$	solid gel, greyish, irreversibel
165	$5.6 \pm 0.1$	not pasty, greyish, inhomogen
180	n.m.	no gel, liquid, white
360	n.m.	kein Gel, flüssig, transparent

### Example 4: Dispersibility of various dextrans

The dextrans produced inventively according to Example 3 (with 40 mmol of HCl at T = 105°C, a holding time of 5 minutes and a heating rate of 8 K/min) were studied with respect to their dispersibility and temperature stability and compared with a commercially available trade product from Avebe (Paselli™-SA 2).

To determine the dispersibility, in each case 2 g of the starch samples were stirred into 100 ml of cold water (25°C). The dispersion, after 1 min, was poured through a 100 µm sieve and the solid content determined in the material passed through (Table 3).

Table 3: Dispersibility of the dextrans

	Paselli™-SA 2	Starch sample B	Starch sample K
Dispersibility	63%	98%	98%

Example 5: Temperature stability of the dextrans

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Table 4 below shows the gel firmness of the inventively produced dextrans (according to Example 3 with  $T = 105^{\circ}\text{C}$ , 5 minutes holding time, heating rate 8 K/min) as a function of the solids content in comparison with a commercially available fat substitute (Paselli™-SA 2 from Avebe).

Tabelle 4: Temperature stability of the dextrans

Dry matter [%]	Gel firmness [N]					
	Paselli™-SA 2		Starch sample B		Starch sample K	
	90°C	120°C	90°C	120°C	90°C	120°C
20	4.3	1.3	2.7	2.8	2.6	0.6
25	11.3	7.4	7.6	13.4	8.6	1.7
30	17.4	14.1	9.0	26.5	13.4	6.1

Table 4 shows a considerably improved thermal stability of the inventive dextrans produced from starch sample B, heated to  $120^{\circ}\text{C}$ .

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Example 6: Acid stability of the gel-formation properties of dextrans

Table 5 below shows the gel firmness of the inventive dextrans (produced according to Example 3 with  $T = 105^{\circ}\text{C}$  and 5 minutes holding time, heating rate 8 K/min) as a function of the pH at a solids content of 20% after heating to  $90^{\circ}\text{C}$  compared with a commercially available fat substituted (Paselli™-SA 2 from Avebe).

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Table 5: pH dependence of gel formation of dextrans

pH	Gel firmness [N]					
	Paselli <sup>TM</sup> -SA 2		Starch sample B		Starch sample K	
2.9	2.3	50%	7.5	82%	3.2	76%
4.0	2.9	63%	9.0	98%	3.3	79%
5.0	3.3	72%	9.1	99%	4.1	98%
6.0	4.6	100%	9.2	100%	4.2	100%

Table 5 shows a markedly improved acid stability of the inventive dextrans produced from starch sample B

T04T20-S1B28260